Infrared spectroscopy of jet-cooled dimers, trimers, and larger clusters

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High resolution spectroscopy of weakly-bound complexes provides a direct and precise experimental probe of intermolecular forces. The ability of theory (quantum chemistry) to calculate reliable intermolecular potentials is rapidly improving, but spectroscopy remains essential for testing theoretical predictions and guiding the development of new methods.

Our spectra are obtained using a tunable mid-infrared laser to probe a pulsed supersonic jet expansion from slit-shaped nozzles. Dilute (<1%) mixtures of the sample molecule(s) in helium carrier gas are used with backing pressures of 3-8 atmospheres, giving effective rotational temperatures of ≈1-4 K. We rely on the versatile PGOPHER program for spectral assignment and simulation [1]. The laser scans a range of ≈1 cm^{-1} at a repetition frequency of ≈1 kHz, with each scan taking about 1 ms and no additional modulation. Jet opening time is a few ms at a pulse rate of a few Hz, limited by vacuum pumping speed. Transmitted laser intensity is recorded after multi-passing through the jet, with the spectrum obtained by subtraction (jet open minus jet shut) and averaged over many pulses. For wavenumber calibration, parts of the laser beam pass through an etalon and reference gas cell. QCL and OPO sources are now used instead of the original Pb-salt diode lasers, bringing advantages of room temperature operation, higher power, and wider tuning. The new sources are mechanically tuned, with less wavenumber agility than diode lasers. We compensate by using sine wave modulation with a lower frequency (≈100 Hz) and larger amplitude, recording only the central 1 ms of the scan (near the sine wave zero-crossing) where it is most rapid and linear. The effective scan rate remains similar (1 cm^{-1}/ms) and the reduced repetition frequency is not a problem since the jet frequency is lower still.

In a recent review, we summarized the spectroscopy of clusters containing (only!) the five small linear molecules N_2O, CO_2, OCS, CS_2, and C_2H_2 [2]. In this talk, results will be presented for $(CO)_2$, $(CO)_3$, CO-N_2, and Rg-benzene complexes (Rg = He, Ne, Ar). This is the first spectroscopic observation of CO trimer, which turns out to have a planar structure with D_{2d} symmetry. Wide band spectra of the CO dimer and CO-N_2 allow many new rotational states to be assigned for these fundamental atmospheric species. The CO dimer absorption extends over a surprisingly large range (≈2135 – 2195 cm^{-1}), and the previously unknown resonant splitting of the upper state ($v_{CO} = 1$) vibrations (symmetric and antisymmetric) is found to be notably small (<0.2 cm^{-1}). Our Rg-C_6D_6 spectra appear to be the first reported for these species in the infrared range. Finally, some published and unpublished results for larger clusters (tetramers, pentamers, ...) will be discussed, including $(CO_2)_N$, $(CS_2)_4$, $(OCS)_4$, $(N_2O)_5$, and $(CO_2)_4$-$(C_2H_2)_2$.

[1] C.M. Western, PGOPHER, a Program for Simulating Rotational Structure, http://pgopher.chm.bris.ac.uk.
[2] N. Moazzen-Ahmadi, A.R.W. McKellar, *International Reviews in Physical Chemistry* **2013**, DOI: 10.1080/0144235X.2013.813799.